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Zirconocene Mediated Acetylboron Chemistry

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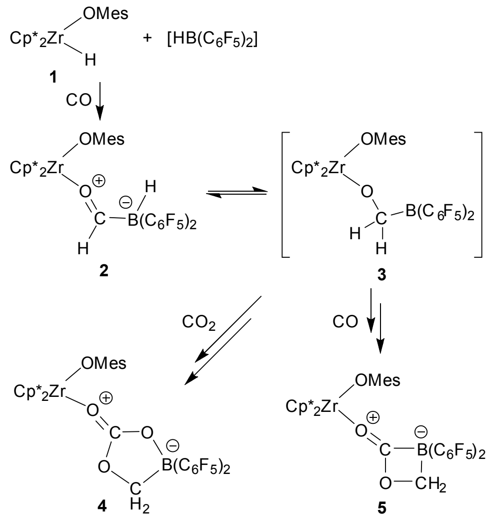
The methyl zirconocene complex $Cp^*_2Zr(Me)OMes$ reacts with methylborane [H_3C-$B(C_6F_5)_2$] and CO to give the respective acetyl(methyl)borate Zr complex. $Cp^*_2Zr(H)OMes$ reacts with H_3C-$B(C_6F_5)_2$ and CO to give the respective acetyl(hydrido)borate Zr product, admixed with a minor amount of the formyl(methyl)borate Zr complex isomer. Prolonged exposure to CO at close to ambient conditions results in uptake of another CO equivalent to yield the corresponding borata-β-lactone zirconocene product.

B_2H_6 does not insert carbon monoxide unless catalyzed. Instead it forms borane carbonyl H_3B-CO under special conditions.[1] Piers' borane [$HB(C_6F_5)_2$][2] behaves analogously. It forms Piers' borane carbonyl $(C_6F_5)_2(H)B$-CO, which we isolated and characterized by X-ray diffraction.[3] Carbon monoxide can be reduced to the formyl stage by $HB(C_6F_5)_2$ either at a frustrated Lewis pair template[4] or with the help of a suitable Lewis acid mediator, e.g. $B(C_6F_5)_3$ or a suitable transition metal complex fragment.[5] We had recently used $Cp^*_2Zr(H)OMes$ for that purpose. We had described that this zirconium hydride complex reduced carbon monoxide in a joint action with $HB(C_6F_5)_2$ to give the Zr-stabilized (hydrido)formyl borate product **2**, which we isolated and characterized by X-ray diffraction and by solid state NMR spectroscopy. We found evidence that in solution compound **2** underwent reversible formyl reduction by the adjacent internal hydridoborate which resulted in endergonic equilibration of **2** with the reactive O/B FLP intermediate **3.** The [Zr]-O-CH_2-[B] system **3** was not directly observed. Evidence of its in situ generation came from the temperature dependent dynamic NMR spectra of compound **2** in solution, and trapping reactions of the reactive intermediate 3 with CO or CO_2 to give the Zr-borata-β-lactone **5** or the Zr-boratacarbonate **4**, respectively (see Scheme 1).[6] Alkylboranes usually react with carbon monoxide. This forms the basis of a number of synthetic protocols for the preparation of alcohols, ketones, aldehydes etc.[7] The alkyl-$B(C_6F_5)_2$ systems seem to mark an exception from the rule. They apparently do not form the formal "CO-insertion" products under the typical conditions.[8] In view of the outcome of the [Zr]H/CO/$HB(C_6F_5)_2$ reactions (see Scheme 1), it was tempting to extend this chemistry to the use of H_3C-$B(C_6F_5)_2$[9] in the Zr-mediated carbonylation reaction. This furnished some surprising results that are described in this account.



Scheme 1 Summary of previously described reactions of the $Cp^*_2Zr(H)OMes$ / $HB(C_6F_5)_2$ mixture with carbon monoxide to give **2** and its follow-up reactions with CO and with CO_2.

We prepared the methyl zirconocene complex **6** by treatment of $Cp^*_2Zr(Me)_2$[10] with the trimethylphenol MesOH (80 °C, 5 d). Compound **6** was isolated as a yellow crystalline product in 75% yield after crystallization from pentane. It was characterized by C,H elemental analysis, NMR spectroscopy [^1H: δ 0.18 ([Zr]-CH_3); δ 6.83 (1H) and 6.75 (1H), δ 2.21 (s, 3H), 2.19 (s, 3H) and

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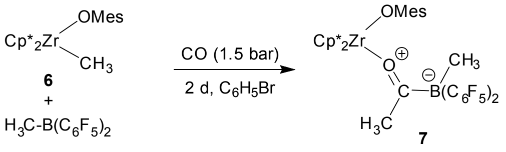
2.07 (s, 3H) O-mesityl] and by X-ray diffraction (the structure is depicted in the ESI).

Compound **6** reacted with $H_3C\text{-}B(C_6F_5)_2$ and carbon monoxide at r.t. (1.5 bar, 2 d, in bromobenzene) to give the zwitterionic [Zr]-acetylborate complex **7** (see Scheme 2). It was isolated as a yellow crystalline solid in 74% yield after crystallization from dichloromethane/pentane. The NMR spectra of compound **7** (in CD_2Cl_2 at 299 K) show the typical set of $^1H/^{13}C$ NMR signals of the [Zr]-OMes group which features hindered rotation around the –O– bonds on the NMR time scale. We monitored the ^{13}C NMR carbonyl signal of the newly formed acetyl group at boron (δ 289.3) and the $^1H/^{13}C$ NMR features of the pair of the methyl groups (δ 2.70/41.6, acetyl; δ 0.50/9.4, [B]-CH_3). Compound **7** shows a ^{11}B NMR signal at δ −12.1 and a small $\Delta\delta^{19}F_{m,p}$ = 3.9 ppm chemical shift difference that is typical of a borate type structure.



Scheme 2 Reaction of the $Cp^*_2Zr(Me)OMes$ / $H_3C\text{-}B(C_6F_5)_2$ mixture with CO

Compound **7** was characterized by an X-ray crystal structure analysis. It contains two independent molecules (**A** and **B**) in the crystal which differ mostly in the conformational arrangement of the acetyl group. Both contain the near to linear [Zr]-O-mesityl arrangement. Both feature the $(CH_3)(C_6F_5)_2B\text{-}C(=O)CH_3$ anion that is oxygen coordinated to the transition metal (see Fig. 1 and Table 1). In the **7A** structure the acetyl methyl group is oriented toward the inside of the σ-ligand plane of the bent metallocene wedge whereas in **7B** it is oriented toward the outside. Aside from that difference both feature typical structural features of a zirconocene cation Lewis acid coordinated carbonyl functionality.

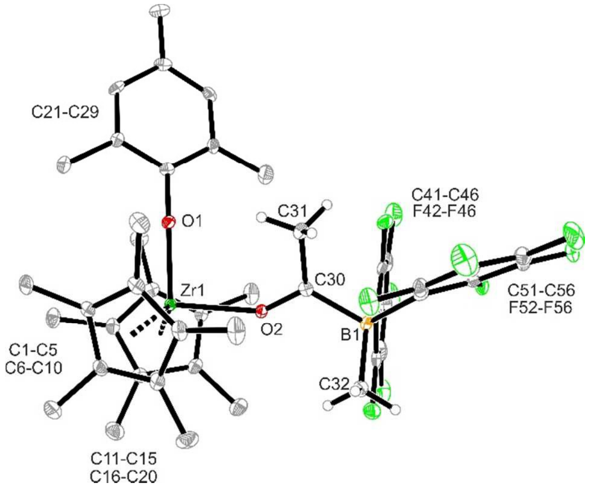


Fig. 1 A view of the molecular structure of the Zr^+ coordinated acetylborate complex **7** (only molecule **A** is shown). Thermal ellipsoids are shown with 30% probability. Most hydrogen atoms have been omitted for clarity.

When we investigated the reaction of the methyl zirconocene complex **6** with $HB(C_6F_5)_2$ and CO we met with a complication. It turned out that upon mixing of **6** with Piers' borane in bromobenzene at r.t. an instantaneous σ-ligand exchange took place. The respective equilibrium lies practically completely on the $Cp^*_2Zr(H)OMes$ (**1**) + $H_3C\text{-}B(C_6F_5)_2$ side (see Scheme 3). Mixing these two components gave identical NMR spectra (see the ESI for the depicted spectra).

The **1** + $H_3C\text{-}B(C_6F_5)_2$ mixture was exposed to carbon monoxide (1.5 bar, 2 d, in bromobenzene). Workup involving crystallization from a CH_2Cl_2/pentane mixture at −35 °C gave the zirconocene acetyl(hydrido)borate complex **9b** as the major product admixed with a minor amount of a second product to which we have ascribed the composition of the zirconocene formyl(methyl)borate complex isomer **9a** (see Scheme 3). The mixture was isolated in 54% yield. The **9b**:**9a** ratio at 299 K is ca. 10:1, it is found increased to ca. 17:1 at 258 K. In CD_2Cl_2 solution (258 K) the major isomer (**9b**) shows a sharp Cp* ^1H NMR signal; it features the typical NMR resonances of the rigid [Zr]-OMes unit. We monitor a broad ^1H NMR [B]H 1:1:1:1 intensity quartet at δ 3.29 (^{11}B NMR: δ −20.4, d, $^1J_{BH}$ = 79.7 Hz) and a singlet of the [B]acetyl group at δ 2.71 [^{13}C NMR: δ 290.1 (C=O)]. The presence of the minor isomer **9a** is detected by its characteristic [B]-formyl ^1H NMR feature at δ 11.56 [^{13}C NMR: δ 274.1 (C=O)] and a small intensity set of the signals of the Cp^*_2Zr-OMes moiety.

Table 1 Selected structural parameters of the zirconocene complexes **7**, **9b** and **13**[a]

compound	**7**[b]	**9b**	**13**
Zr1–O1	1.978(3)	1.981(2)	1.973(2)
Zr1–O2	2.200(2)	2.164(2)	2.177(2)
O2–C30	1.271(4)	1.257(3)	1.247(3)
O1–C21	1.369(5)	1.361(3)	1.366(3)
C30–C31	1.497(6)	1.490(3)	1.328(3)[c]
B1–C30	1.663(6)	1.625(4)	1.652(4)
B1–C32	1.620(6)	–	1.647(3)[d]
O1–Zr1–O2	96.1(1)	99.0(1)	95.4(1)
Zr1–O1–C21	165.3(2)	178.6(2)	169.9(2)
Zr1–O2–C30	146.0(3)	166.1(2)	137.1(2)
O1–Zr1–O2–C30	33.4	-135.5	176.2
O2–C30–B1–C32	-50.6(4)	–	175.5(3)[e]

[a] Bond lengths in Å, angles in deg. [b] data of molecule A. [c] C30–O3. [d] B1–C31. [e] O2–C30–B1–C31.

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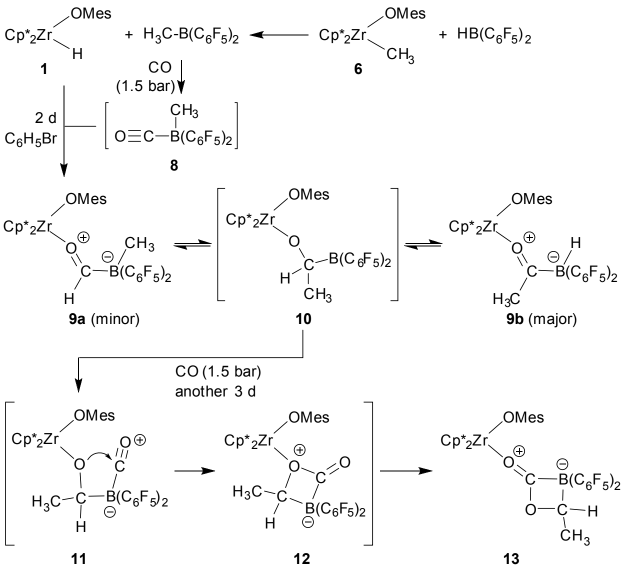

Scheme 3 Reactions of the $Cp^*_2Zr(H)OMes$ / $H_3C\text{-}B(C_6F_5)_2$ mixture with CO

Crystallization from a 5:1 pentane/CH_2Cl_2 mixture at −35 °C gave single crystals of the major isomer **9b** suited for the X-ray crystal structure analysis (see Fig. 2 and Table 1). It features the acetyl(hydrido)borate moiety O-coordinated at the formal $Cp^*_2Zr(OMes)^+$ cation template. In the crystal we find an orientation of the acetyl methyl group toward the outside at the bent metallocene wedge.

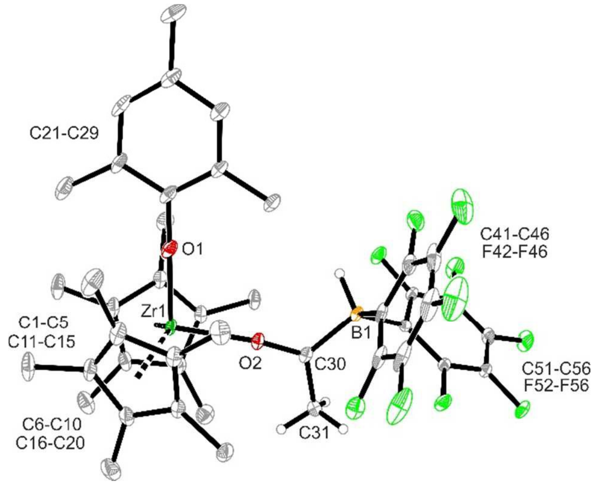

Fig. 2 A view of the molecular structure of the zirconocene acetylborate complex **9b** (major isomer). Thermal ellipsoids are shown with 30% probability. Most hydrogen atoms have been omitted for clarity.

We assume that the compounds **9** are formed out of the **1**/**6** equilibration by means of nucleophilic hydrido zirconium attack at the $(C_6F_5)_2(CH_3)B\text{-}CO$ borane carbonyl (**8**). In this pathway the formyl(methyl)borate Zr complex **9a** would be formed first. This minor isomer might then equilibrate with the observed (and crystallographically characterized) major isomer, the acetyl(hydrido)borate Zr complex **9b** via the intermediate **10**. This we could not observe directly, but we were able to trap it by making use of its incipient oxygen/boron FLP character.

The alleged reactive O/B FLP **10** intermediate was successfully trapped with carbon monoxide. For this purpose we exposed the $Cp^*_2Zr(H)OMes$ (**1**)/$H_3C\text{-}B(C_6F_5)_2$ mixture in bromobenzene for 5 d at r.t. to a carbon monoxide atmosphere (at 1.5 bar). Workup involving crystallization from a dichloromethane/pentane mixture furnished complex **13** as a yellow crystalline solid, which was isolated in 48% yield. It was characterized by C,H elemental analysis, by NMR spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis (see Fig. 3 and Table 1) revealed the formation of a borata-β-lactone moiety. It contains a methyl substituent at the sp^3 ring carbon atom and it is connected to the formally cationic $Cp^*_2Zr(OMes)$ template through the ester carbonyl oxygen atom. The bent metallocene complex features a conformational orientation with the ring oxygen atom pointing to the outside in the Cp*-Zr-Cp* bisecting bent metallocene plane.

Complex **13** contains a carbon chirality center inside the boratalactone ring. Consequently, it shows a pair of Cp* methyl ^{1}H NMR singlets in CD_2Cl_2 solution at 299 K and two equal intensity sets of ^{19}F NMR resonances of the pair of diastereotopic C_6F_5 substituents at boron. The ^{11}B NMR feature of compound **13** occurs at δ −9.9. The Zr^+-coordinated lactone carbonyl shows a ^{13}C NMR resonance at δ 215.2 and we observed the typical ^{1}H NMR pattern of the ring $CH\text{-}CH_3$ moiety [δ 5.30 (q, 1H), 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 3H)] (for further details see the ESI).

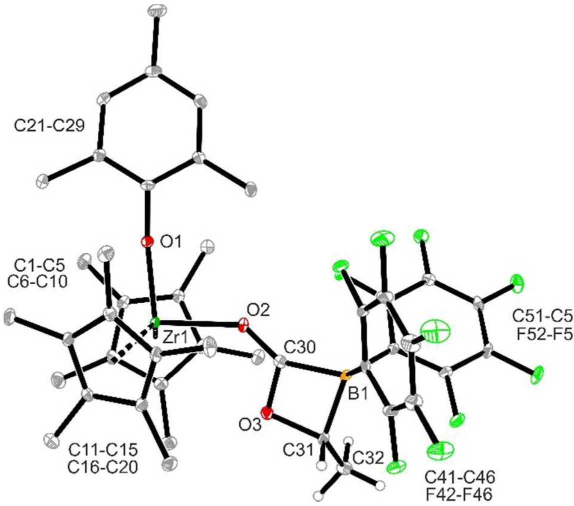

Fig. 3 Molecular structure of the borata-β-lactone Zr complex **13**. Thermal ellipsoids are shown with 30% probability. Most hydrogen atoms have been omitted for clarity.

We assume a pathway of the formation of complex **13** as it is tentatively formulated in Scheme 3. This would involve bonding of CO to the Lewis acidic borane to generate the reactive intermediate **11** which is set for internal nucleophilic attack by the adjacent FLP oxygen atom to form the borata-β-lactone moiety in **12**. Rearrangement to give the preferred Zr^+ to carbonyl oxygen coordination would then directly lead to the observed product **13** (see Scheme 3).

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In summary, our study has revealed a common pattern in the carbonylation reactions involving the Cp*$_2$Zr(OMes)-H/-CH$_3$, H$_3$C-/H-B(C$_6$F$_5$)$_2$ pairs of reagents. It seems that the borane is used for CO activation which then subsequently allows nucleophilic attack by the Zr-H/Zr-CH$_3$ nucleophiles. We also note that in the cases investigated a facile reversible generation of the respective [Zr]-O-CH(R)-[B] isomer was indirectly detected, which served as a reactive frustrated O/B Lewis pair. In a related metal free case we could recently even isolate a respective derivative.[8] In the cases studied so far these types of O/B FLPs reacted with carbon monoxide to give the borata-β-lactone systems which indicated a unique reactivity of such active oxygen/boron compounds.

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Conflicts of interest

There are no conflicts to declare.

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Text for TOC:

Carbon monoxide reacts with a zirconium hydride and the borane methyl-B($_6$F$_5$)$_2$ to give a Zr-bound acetyl(hydrido)borate as the major product. This reacts further with CO to form a Zr-coordinated borata-β-lactone.

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